

Catalytic abatement of acetaldehyde over oxide-supported precious metal catalysts

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Abstract

Catalytic combustion of acetaldehyde was investigated on various oxide-supported metal catalysts prepared by impregnation method. Among the as-calcined catalysts tested, SnO₂-supported precious metal catalysts showed the highest activity at low temperatures despite low BET surface area, whereas the catalytic activity of the SnO₂-supported samples was significantly degraded by reduction treatment in H₂ atmosphere. The catalytic activity of ZrO₂- and CeO₂-supported metal catalysts was improved by reduction treatment, as compared with the as-calcined catalysts. Among the reduced catalysts, ZrO₂-supported metal catalysts exhibited the highest activity for acetaldehyde combustion. To reveal these phenomena, all the catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and BET surface area. The catalytic activity was strongly related to the surface species easily reducible at low temperatures. Over the as-calcined SnO₂-supported catalysts, Pt particles were highly dispersed and the existence of platinum species reducible at room temperature was inferred from XPS and TPR, which disappeared by the H₂ reduction treatment, leading to deterioration of the activity. On the other hand, over the ZrO₂- and CeO₂-supported samples, precious metal species were reduced to metallic state by the H₂ reduction treatment and stabilized to maintain the enhanced catalytic activity under oxidative atmosphere during acetaldehyde combustion.

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1. Introduction

Volatile organic compounds (VOCs) have relatively high vapor pressure under ambient conditions so that they are easily vaporized when emitted into atmosphere. VOCs are recognized as air pollutants that cause photochemical smog, ground-level ozone, sick house syndrome, and chemical sensitivity [1–3]. Therefore, efficient techniques for VOCs abatement are required, and various methods such as catalytic combustion, flame combustion, catalytic decomposition using ozone and plasma, microwave-driven methods, adsorbent-based methods, and so on, have been intensively investigated [4–8]. Among these methods, catalytic combustion has advantageous features for VOCs removal that complete combustion of dilute fuel

proceeds stably at low temperatures, and thus extremely low emission of NO_x and unburned fuels can be achieved [9].

A wide variety of supported precious metal catalysts has been reported to exhibit high activity for the catalytic combustion of VOCs. It is well known that reduction treatment greatly affects catalytic activity, since active species and support materials interact strongly each other [10–16]. Thus, the support materials play important roles in catalytic combustion. In general, metal oxides with high surface area and thermal stability, such as γ -Al₂O₃, TiO₂, CeO₂, and ZrO₂, are selected as support materials to disperse active species. Recently, we have reported Pd/SnO₂ exhibited much higher activity for methane combustion in comparison with Pd/ γ -Al₂O₃ despite the extremely low surface area ($S_{\text{BET}} = 4.9 \text{ m}^2 \text{ g}^{-1}$) [17,18]. Further, it was also found that catalytic activity of Pt/SnO₂ for methane combustion was comparable to that of Pd/SnO₂ [19]. These prominent features can be derived from a strong chemical interaction between precious metal and SnO₂. Due to the unusual characteristics of the SnO₂-supported metal catalysts, they are expected to have a

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great potential for VOC combustion. Nevertheless, few studies have been conducted so far [20,21].

The aim of the present work is to develop catalysts with high combustion efficiency for VOCs at low temperatures. As a model VOC, acetaldehyde was employed, because it is widely used as a raw material of various organic compounds in spite of high volatility at room temperature, and the regulation against acetaldehyde emission will be carried out near future. Platinum and palladium were supported on several oxides, and the effects of preparation conditions including H_2 reduction treatment were investigated for acetaldehyde combustion activity.

2. Experimental

2.1. Catalyst preparation

Oxide-supported metal catalysts were prepared by impregnation method. SnO_2 (Wako Pure Chemical), ZrO_2 (RC-100, Daiichi Kigenso Kagakukogyo), and CeO_2 (Aldrich) were selected as support materials. Prior to soaking, SnO_2 powder was calcined at 800 °C for 5 h, whereas others were used without any pretreatments. Solution of $Pt(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo) or $Pd(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo) was used as a precious metal source. Support materials were impregnated with the solutions. The mixture was kept on a steam bath at 80 °C until the solution was evaporated. Subsequently, the resultant powder was calcined at 400 °C for 30 min in air. Metal loadings in the impregnated oxide-supported metal catalysts were 1.0 and 10 wt.% in every case. Part of as-calcined catalysts was heat-treated at 400 °C for 15 min in 50% H_2/N_2 prior to characterization and catalytic reactions.

2.2. Catalytic combustion of acetaldehyde

A fixed-bed flow reactor made of quartz tubing of 8 mm inner diameter was used, and the prepared catalyst (600 mg) was set in the reactor. All catalysts were tabletted and pulverized into 10–26 mesh before catalytic reaction tests. A gaseous mixture composed of 1.0% CH_3CHO and 99.0% air was fed at a flow rate of 100 ml min^{-1} (space velocity: 10,000 l $kg^{-1} h^{-1}$). The temperature was raised from room temperature to 350 °C at a heating rate of 100 °C h^{-1} . Products were analyzed by an on-line micro-gas chromatograph (VARIAN, CP-4900). A PoraPLOT Q column was used for separation of acetaldehyde and CO_2 (carrier gas: He, column temperature: 60 °C).

2.3. Catalyst characterization

The samples with 10 wt.% metal loadings were used to clarify the changes in crystalline phase and electronic state of precious metals. The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and BET surface area. XRD patterns were recorded by using Cu $K\alpha$ radiation on a RIGAKU Rint 2500 diffractometer for phase identification in

the samples. XPS measurements were conducted on Shimadzu ESCA-850 using a Mg $K\alpha$ source. In the case of reduced catalysts, the samples were transferred directly into XPS chamber without exposure to air after reduction treatment. The binding energy was referenced to the C 1s peak (285.0 eV). BET surface area was measured by N_2 adsorption at the liquid nitrogen temperature using a Shimadzu Gemini 2375 analyzer. TPR measurements were performed in a quartz tube reactor, and the amount of consumed hydrogen was measured by a thermal conductivity detector (TCD). A weighed amount (25 mg) of the as-calcined catalysts was placed in the reactor, and then a gaseous mixture of 5% H_2 –95% Ar was fed to the reactor at 30 ml min^{-1} . The temperature was raised to 800 °C at a heating rate of 10 °C min^{-1} . The amount of H_2 detected by TCD was calibrated by the consumption of H_2 for the reduction of CuO (Merck).

The size and dispersion of supported metal particles was determined from the uptake of CO on the surface. The adsorption was carried out by O_2 – CO_2 – H_2 –CO pulse method, since the conventional method is inapplicable to the supports with large oxygen storage capacity due to overestimation of CO adsorbed [22]. First, the sample was heat-treated at 300 °C in oxygen atmosphere, and then cooled down to room temperature, and subsequently this sample was reduced at 400 °C for 10 min in hydrogen atmosphere and cooled down to room temperature. Next, O_2 , CO_2 , and H_2 gas was fed to the sample in sequential manner at room temperature for 5 min, and 0.244 ml of CO was pulsed to the sample until the intensity of the peak reached a constant value.

3. Results and discussion

3.1. Acetaldehyde combustion of the as-calcined catalysts

The support effect of oxide-supported Pt catalysts was examined for acetaldehyde combustion. The results of the catalytic activity tests over as-calcined Pt/ SnO_2 , Pt/ ZrO_2 , and

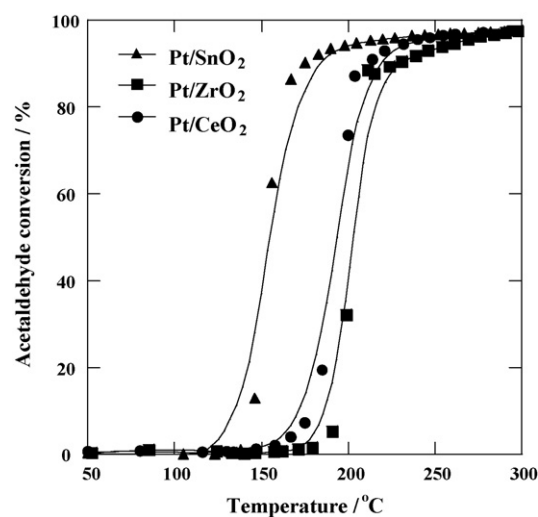


Fig. 1. Acetaldehyde conversion over oxide-supported 1.0 wt.% Pt catalysts. Reaction conditions: acetaldehyde, 1.0%; air, 99.0%; S.V. = 10,000 l $kg^{-1} h^{-1}$; heating rate, 100 °C h^{-1} .

Table 1

Surface area and catalytic activity for acetaldehyde oxidation of oxide-supported 1.0 wt.% metal catalysts

Catalyst	Surface area (m ² g ⁻¹) ^a	Catalytic activity ^b		
		<i>T</i> ₁₀ (°C)	<i>T</i> ₅₀ (°C)	<i>T</i> ₉₀ (°C)
Pt/SnO ₂	5.4	135	155	180
Pt/ZrO ₂	94.6	190	200	220
Pt/CeO ₂	69.5	170	190	210
Pd/SnO ₂	6.0	190	205	230
Pd/ZrO ₂	92.4	200	220	235
Pd/CeO ₂	72.3	175	220	300

^a Measured by the BET method.

^b Temperature at which acetaldehyde conversion levels are 10, 50, and 90%, respectively.

Pt/CeO₂ are shown in Fig. 1. Almost all acetaldehyde was completely oxidized in every case because only carbon dioxide and water were detected as reaction products. Among the catalysts, Pt/SnO₂ exhibited the highest activity; ignition temperature was 120 °C, and the conversion of 90% was attained at 180 °C. Catalytic activity and surface area of various oxide-supported metal catalysts are summarized in Table 1. The catalytic activity was characterized by the temperature where acetaldehyde conversion reached 10, 50, and 90%, as expressed by *T*₁₀, *T*₅₀, and *T*₉₀, respectively. The effect of the support materials on the catalytic activity of Pd catalyst is quite similar, Pd/SnO₂ showed the highest activity at low temperatures despite low BET surface area. Considering the active species, platinum exhibited better activity for acetaldehyde oxidation, independent of the support materials.

3.2. Characterization of the as-calcined catalysts

Then, TPR analysis was conducted so as to reveal the difference in catalytic activity, and the results are shown in Fig. 2. The TPR profiles of Pt/ZrO₂ consisted of two main peaks observed at *ca.* 210 and 300 °C, while zirconia itself is almost irreducible. The former and latter peaks are attributed to the reduction of platinum oxide and the promoted support reduction through spillover of hydrogen species from Pt onto ZrO₂ [23], respectively. The profiles of Pt/CeO₂ exhibited three peaks at low and high temperatures (155, 400, and 480 °C). The peak at *ca.* 155 °C corresponds to the platinum oxide reduction, and the other two peaks at high temperatures are ascribed to the reduction of the surface capping oxygen of CeO₂ [24]. The reduction of platinum oxide started at lower temperature over Pt/CeO₂ than Pt/ZrO₂, and Pt/CeO₂ displayed higher activity for acetaldehyde oxidation as shown in Fig. 1. Accordingly, platinum species reducible at lower temperatures should be active for oxidation of acetaldehyde. As Pt loading increased, the reduction peaks of platinum oxide were broadened for both Pt/ZrO₂ and Pt/CeO₂. The H₂ uptakes are summarized in Table 2, determined from the TPR profiles by assuming the reduction of PtO to Pt. It was found that the experimentally determined H₂ uptake was almost 10 times larger than that needed for complete platinum reduction of the samples with 1.0 wt.% Pt loaded, whereas over the 10 wt.% Pt-loading

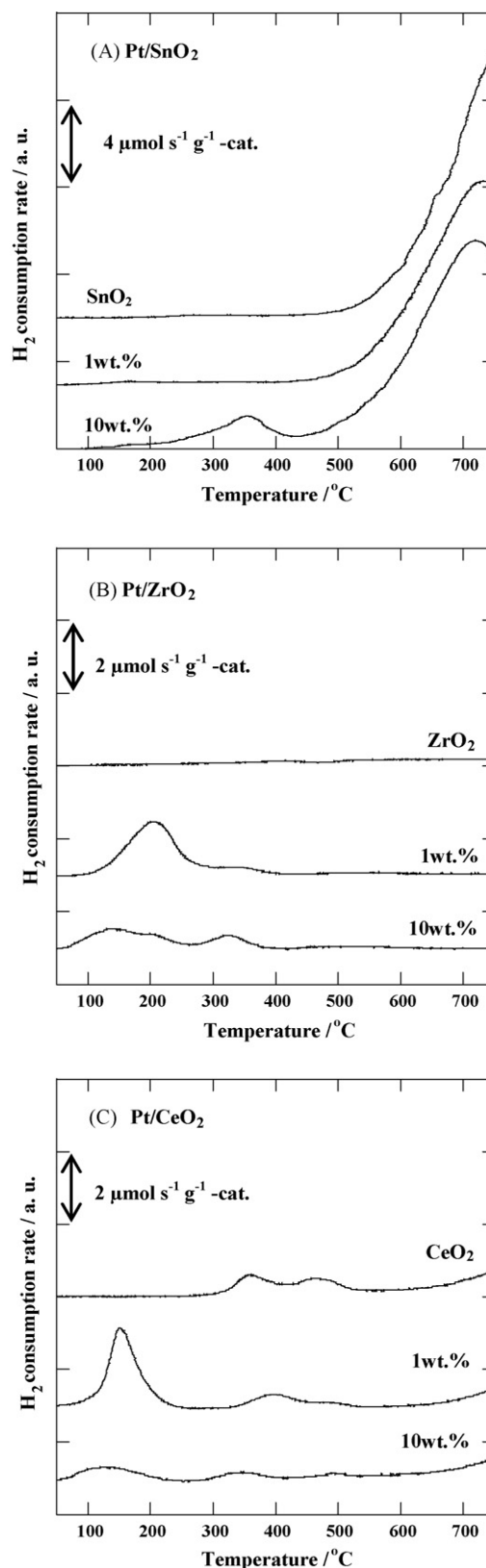


Fig. 2. TPR profiles of oxide-supported Pt catalysts: (A) Pt/SnO₂, (B) Pt/ZrO₂, and (C) Pt/CeO₂.

Table 2

H₂ uptake determined from the reduction peaks of platinum oxide on Pt/ZrO₂ and Pt/CeO₂

Sample	H ₂ uptake ($\times 10^{-4}$ mol g ⁻¹)	Theoretical value ($\times 10^{-4}$ mol g ⁻¹)
1 wt.% Pt/ZrO ₂	7.37	0.513
1 wt.% Pt/CeO ₂	7.37	0.513
10 wt.% Pt/ZrO ₂	5.33	5.13
10 wt.% Pt/CeO ₂	1.69	5.13

Table 3

Particle size and dispersion of platinum on ZrO₂ and CeO₂

Sample	Pt particle diameter (nm)	Dispersion (%)
1 wt.% Pt/ZrO ₂	2.2	52.6
1 wt.% Pt/CeO ₂	4.2	26.5
10 wt.% Pt/ZrO ₂	10.4	10.9
10 wt.% Pt/CeO ₂	5.7	19.9

samples the experimental and theoretical H₂ uptakes were comparable. The size and dispersion of platinum on ZrO₂ and CeO₂ supports are summarized in Table 3. In the case of 1.0 wt.% Pt-loading samples, the small particles of platinum were deposited on the supports in highly dispersed state. When Pt loading increased, however, Pt particle size was increased, leading to lower Pt dispersion. These results indicate that when Pt particles are small and well dispersed, in addition to the complete reduction of platinum oxide, zirconia can be reduced at the metal interface. On the other hand, as the Pt loading increased to 10 wt.% Pt particles grew in size probably due to agglomeration. Peak broadening as well as multiple peaks on the TPR profiles for 10 wt.% Pt-loading samples suggest that distribution of Pt particle size became broad as the Pt loading increased.

In contrast, the profiles of Pt/SnO₂ were quite different from the others. A broad peak attributed to the reduction of SnO₂ appeared above 500 °C, and the onset temperature has lowered with an increase in Pt loadings. In the case of 1.0 wt.% Pt/SnO₂, a reduction peak of platinum oxide was not detected, and when the Pt loading was increased up to 10 wt.%, a small peak appeared at around 350 °C. It is highly likely that there exists platinum oxide species that can be reduced below 100 °C, possibly during pretreatment by H₂ at room temperature, as in the case of Pd/SnO₂ [18]. This is consistent with XPS results shown in later Table 5 that platinum species should be in oxidized state after the calcinations in air. The appearance of the small peak in the TPR profile of 10 wt.% Pt/SnO₂ indicates that the amount of platinum species interacting weakly with SnO₂ increased when the Pt loading was raised. The surface area of Pt/SnO₂ and Pd/SnO₂ as a function of metal loadings are shown in Fig. 3A. The surface area of Pt/SnO₂ is proportional to metal loadings, whereas that of Pd/SnO₂ is almost unchanged even at 20 wt.% loading. In addition, the metal particle size of the catalysts was calculated from the surface area by assuming that the particles were spherical. As shown in Fig. 3B, the calculated Pd particle size of Pd/SnO₂ increases consistently with metal loadings, while that of Pt/SnO₂ is constant at ca.

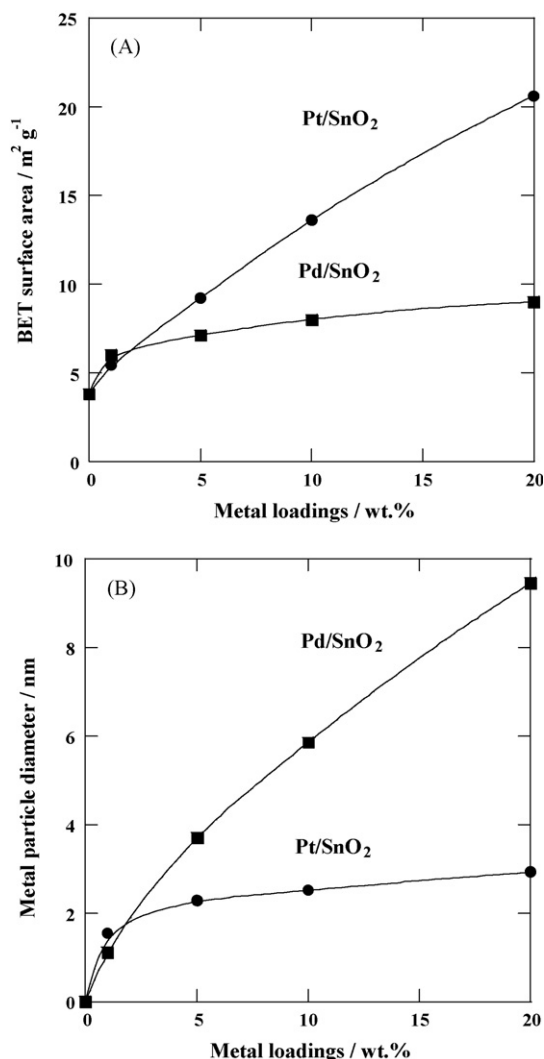


Fig. 3. (A) BET surface area and (B) metal particle diameter of SnO₂-supported metal catalysts with various metal loadings.

3 nm even at 20 wt.% loadings. This suggests that Pt particles are highly dispersed on SnO₂.

3.3. Effect of reduction treatment

3.3.1. Acetaldehyde combustion of reduced catalysts

Considering the TPR profiles, the supported metal particles can be reduced completely above 400 °C. After as-calcined catalysts were reduced at 400 °C for 15 min in hydrogen atmosphere, acetaldehyde combustion was examined. As shown in Fig. 4, the reduction treatment has significantly affected the activity of oxide-supported Pt catalysts. The reduced Pt/ZrO₂ exhibited the highest activity although the activity of as-calcined one was the lowest. The turnover frequency ($16.3 \times 10^{-3} \text{ s}^{-1}$) of Pt/ZrO₂ at 120 °C was higher than that of Pt/CeO₂ ($9.03 \times 10^{-3} \text{ s}^{-1}$). Catalytic activity of the various oxide-supported metal catalysts after reduction treatment is summarized in Table 4. The catalytic activities of ZrO₂- and CeO₂-supported metal catalysts are improved by reduction treatment as compared with the as-calcined catalysts.

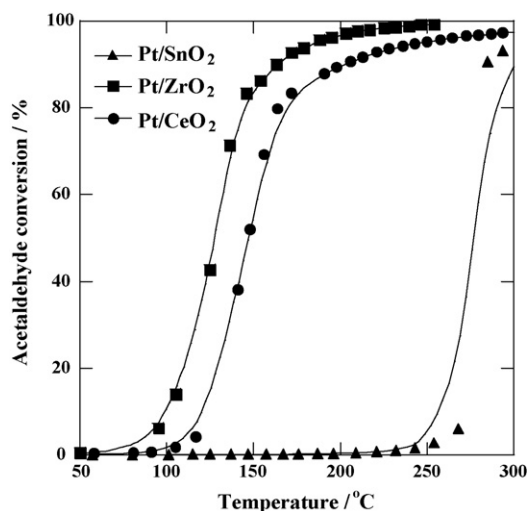


Fig. 4. Acetaldehyde conversion over oxide-supported 1.0 wt.% Pt catalysts reduced at 400 °C. Reaction conditions: acetaldehyde, 1.0%; air, 99.0%; S.V. = 10,000 l kg⁻¹ h⁻¹; heating rate, 100 °C h⁻¹.

The enhancement of the activity was more evident over ZrO₂- and CeO₂-supported Pt catalysts than Pd catalysts. This is because PdO_x can be relatively active for acetaldehyde combustion, as in the case of hydrocarbon combustion [25–27]. On the other hand, the activity of SnO₂-supported metal catalysts was significantly degraded by the reduction treatment. The conversion increased abruptly from 270 °C. Thus, the effect of reduction treatment differs depending on the supports, and in the following section the effect will be elucidated.

3.3.2. Characterization of reduced catalysts

Upon the reduction treatment, the catalytic activity of SnO₂-supported metal catalysts was significantly degraded. The characterization of catalysts was carried out before and after the reduction treatment. The XRD patterns of 10 wt.% Pt/SnO₂, Pt/ZrO₂, and Pt/CeO₂ are shown in Fig. 5. In the patterns of the as-calcined samples (Fig. 5A), the lines were consistent with SnO₂, ZrO₂, and CeO₂. However, no lines ascribable to Pt were observed, suggesting that the size of platinum crystallites is too small to be detected [28]. Even after the reduction treatment, the diffraction patterns of Pt/ZrO₂ and Pt/CeO₂ remained unchanged. On the other hand, the pattern of reduced Pt/SnO₂ was significantly changed and contained the new phase attributed to PtSn (Fig. 5B). Since the intensity of the lines from SnO₂ decreased in comparison to that of the as-calcined

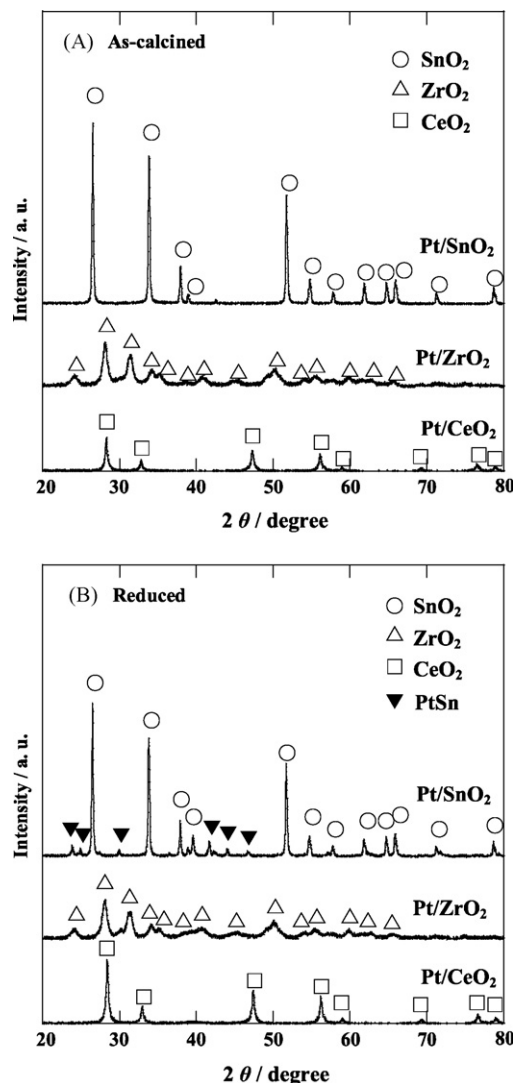


Fig. 5. XRD patterns of oxide-supported 10 wt.% Pt catalysts: (A) As-calcined and (B) Reduced.

sample, an intermetallic compound should be produced by solid state reaction between Pt and SnO₂. As shown in Fig. 6, the formation of an intermetallic compound was also observed on Pd/SnO₂: the pattern of reduced Pd/SnO₂ contained the new phase ascribable to Pd₃Sn₂.

The XPS analysis of Sn 3d_{5/2} on SnO₂-supported metal catalysts before and after reduction treatment is shown in Fig. 7, respectively. For both Pt/SnO₂ and Pd/SnO₂, the peak attributed to SnO₂ is negatively shifted, and a shoulder peak (485.0 eV) appears. The shoulder peak is consistent with binding energy of Sn⁰ (Sn 3d_{5/2} = 485.0 eV [29]), indicating that SnO₂ was partially reduced by reduction treatment. We have previously reported that Pt particles on Pt/SnO₂ surface scarcely adsorbed CO after reduction treatment at 400 °C as a result of peculiar core-shell structure formation [30]. The core-shell structure is formed in the following manner; tin component at the surface of intermetallic compound is oxidized when exposed to air. In this study, all the catalytic combustion of acetaldehyde was conducted in air. Thus, the deactivation of Pt/SnO₂ and Pd/SnO₂ by reduction treatment is ascribable to the formation of

Table 4

Surface area and catalytic activity for acetaldehyde oxidation of oxide-supported 1.0 wt.% metal catalysts reduced at 400 °C

Catalyst	Surface area (m ² g ⁻¹)	Catalytic activity		
		T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
Pt/SnO ₂	4.8	260	280	300
Pt/ZrO ₂	91.1	100	130	165
Pt/CeO ₂	63.6	120	145	200
Pd/SnO ₂	5.1	285	300	320
Pd/ZrO ₂	89.6	130	190	210
Pd/CeO ₂	64.5	145	190	230

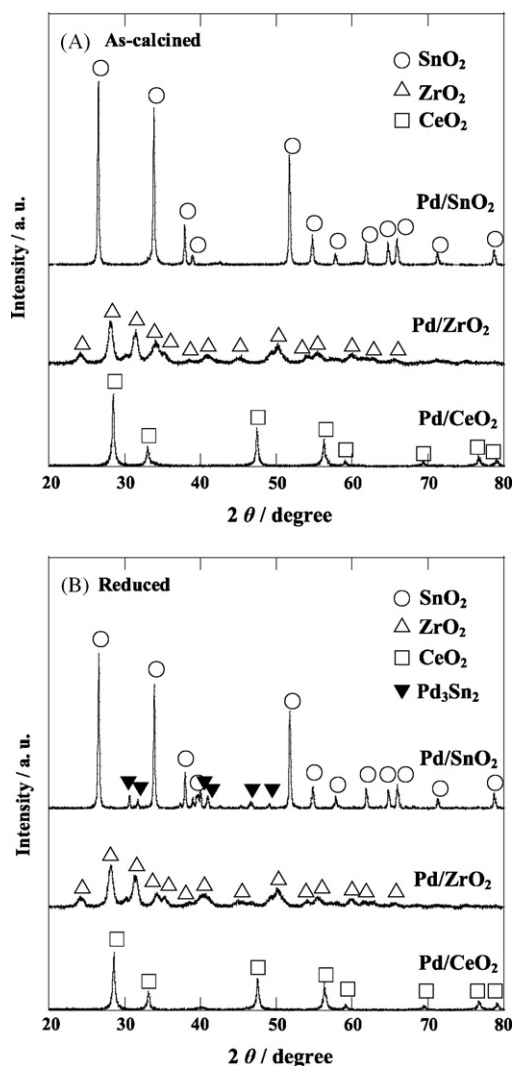


Fig. 6. XRD patterns of oxide-supported 10 wt.% Pd catalysts: (A) As-calcined and (B) Reduced.

intermetallic compounds, and subsequent oxidation of tin species at the most outer surface. This should result in the inhibition of acetaldehyde adsorption.

The catalytic activity of ZrO₂- and CeO₂-supported metal catalysts was improved by reduction treatment. To reveal these phenomena, the electronic state of supported metal was investigated from the binding energy. The results of XPS analysis are summarized in Table 5. The binding energy of Pt 4f_{7/2} and Pd 3d_{5/2} was recorded in every case. The binding energy of the as-calcined catalysts was almost equal to the reported value of precious metals in oxidized state: PtO (Pt 4f_{7/2} = 73.8 eV) and PdO (Pd 3d_{5/2} = 336.3 eV) [29]. On the other hand, the reduced catalysts exhibited binding energy almost identical to that of Pt⁰ (Pt 4f_{7/2} = 71.2 eV) and Pd⁰ (Pd 3d_{5/2} = 335.1 eV), respectively [29].

3.3.3. Stability test of reduced catalysts

Among the catalysts, the reduced ZrO₂-supported metal catalysts exhibited higher activity as shown in the previous section. The stability of the activity was studied at *ca.* 200 °C as

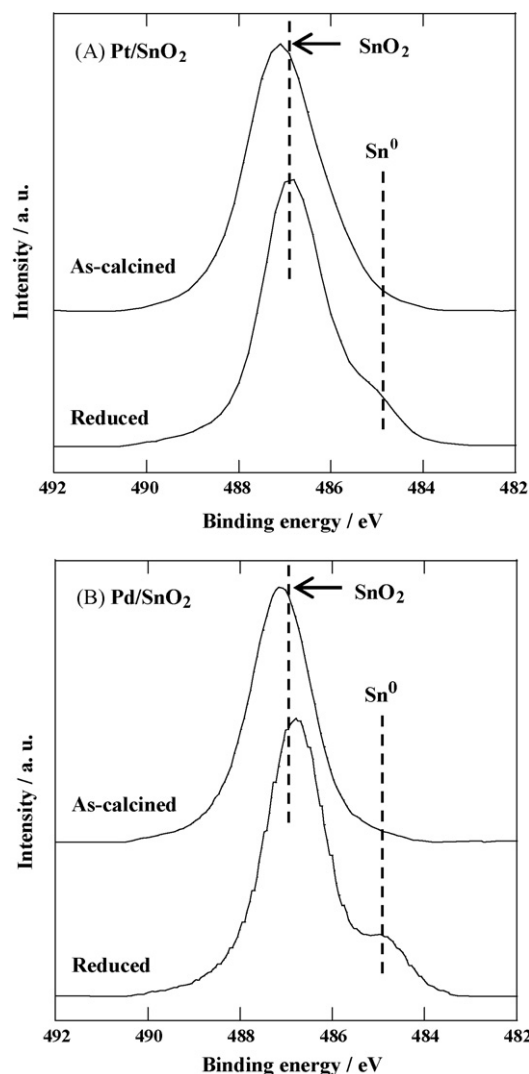


Fig. 7. XPS spectra for Sn 3d_{5/2} of SnO₂-supported 10 wt.% metal catalysts: (A) Pt/SnO₂ and (B) Pd/SnO₂.

shown in Fig. 8. Both reduced Pt/ZrO₂ and Pd/ZrO₂ maintained stable behavior during acetaldehyde combustion for 30 h with a conversion of *ca.* 100%. Then, the XPS analysis was conducted for Pt/ZrO₂ and Pd/ZrO₂, as shown in Fig. 9A and B, respectively. In the spectra of Pt/ZrO₂, the two peaks at high and low binding energy are corresponding to Pt 4f_{5/2} and Pt 4f_{7/2}, respectively. It is apparent that the both peaks are negatively shifted by reduction treatment. Regardless of the subsequent

Table 5
Binding energy of oxide-supported 10 wt.% metal catalysts

Sample	Binding energy/eV	
	As-calcined	Reduced
Pt/SnO ₂ ^{a)}	74.7	71.7
Pt/ZrO ₂ ^{a)}	72.4	71.3
Pt/CeO ₂ ^{a)}	72.9	71.1
Pd/SnO ₂ ^{b)}	337.3	336.0
Pd/ZrO ₂ ^{b)}	336.7	–
Pd/CeO ₂ ^{b)}	337.1	335.1

Binding energy is value of (a) Pt 4f_{7/2} and (b) Pd 3d_{5/2}.

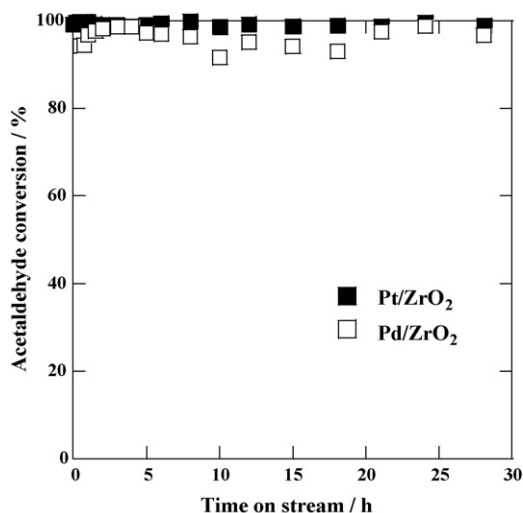


Fig. 8. Time course of the catalytic activity over 1.0 wt.% Pt/ZrO₂ and Pd/ZrO₂ reduced at 400 °C. Reaction conditions: acetaldehyde, 1.0%; air, 99.0%; S.V. = 10,000 l kg⁻¹ h⁻¹; T = 200 °C.

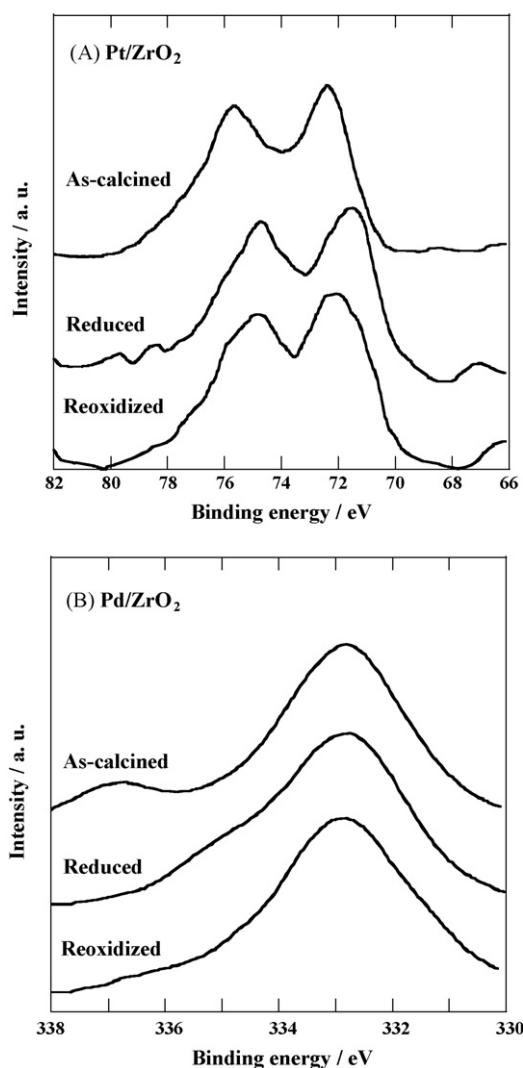


Fig. 9. XPS spectra of ZrO₂-supported 10 wt.% metal catalysts: (A) Pt 4f spectra of Pt/ZrO₂ and (B) Pd 3d_{5/2} spectra of Pd/ZrO₂.

reoxidation treatment of the reduced samples at 200 °C; however, the peak position was slightly shifted to positive side but not to the initial level. Thus, the precious metals in metallic state should be responsible for the high catalytic activity. This result agrees well with TPR measurements. In the case of Pd/ZrO₂, similar behavior was observed. The binding energy of Pd 3d_{5/2} peak at *ca.* 337 eV is negatively shifted by the reduction treatment, resulting in the appearance of shoulder peaks at *ca.* 335 eV. Further, the reoxidation treatment has not led to the significant change in the spectra. These results suggest that precious metal species are stabilized in the reduced state even under the oxidizing atmosphere, resulting in the stable behaviors during acetaldehyde combustion.

4. Conclusions

Various oxide-supported metal catalysts were investigated for low-temperature oxidation of VOCs. As a typical example of VOCs, acetaldehyde was used. Among the as-calcined catalysts, Pt/SnO₂ exhibited the highest activity despite extremely low surface area. The supported Pt particles were highly dispersed on SnO₂ support. However, over the SnO₂-supported metal catalysts, an intermetallic compound was formed by reduction treatment, and the activities were significantly degraded. In the case of ZrO₂- and CeO₂-supported metal catalysts, the supported metal particles existed in metallic state by reduction treatment, resulting in the improvement in activity. Among the reduced catalysts, ZrO₂-supported metal catalysts exhibited the highest activity for acetaldehyde combustion and maintained stable activity during acetaldehyde combustion for 30 h at a conversion of *ca.* 100%. This result suggests that the supported metal particles were stabilized in the reduced state even under the oxidizing atmosphere.

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